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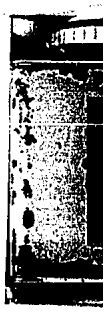

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THE ACTION OF CARBON TETRACHLORIDE ON ALKYL ESTERS OF PYROPHOSPHOROUS ACID

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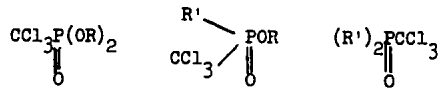
Submitted by Acad A. Ye. Arbuzov
2 Nov 1949

In 1935, I (1) established for the first time that carbon tetrachloride reacts with alkyl esters of phosphorous acid and that it is not an indifferent solvent.

As a result of the systematic investigations which were carried out along those lines, new representatives of esters of trichloromethylphosphoric acids and oxides of diaryl trichloromethylphosphine were synthesized from the following general types:



where R is CH_3, C_2H_5, C_3H_5, C_3H_7, C_4H_9 and R' is C_6H_5, n-$CH_3C_6H_4$, n-CH_3-OC_6H_4.

In the brief report below, the action of carbon tetrachloride on ethyl, n-propyl, and n-butyl esters of pyrophosphorous acid is described.

In 1930, A. Ye. Arbuzov and B. A. Arbuzov (2) studied the reaction of triphenyl bromomethane on the ethyl ester of pyrophosphorous acid, in which the ethyl ester of pyrophosphorous acid, as the derivative of two trivalent phosphorus atoms, underwent a complex transformation with triphenyl bromomethane according to the following scheme:

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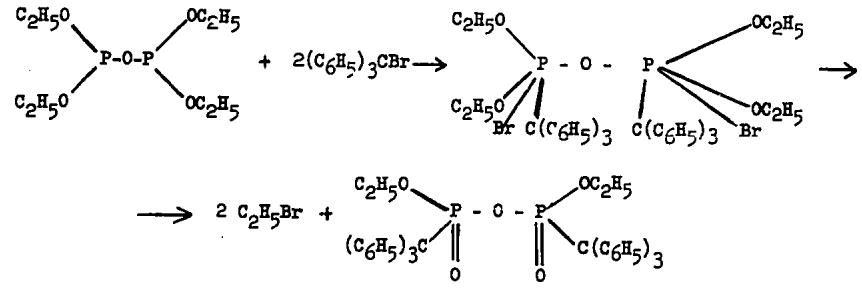
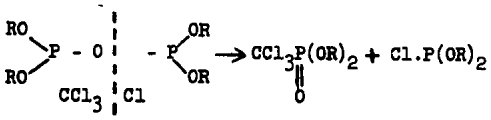


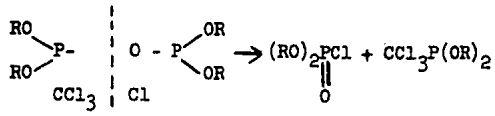
Analogous transformations of esters of phosphorous acids with other alkyl halides have been investigated in A. Ye. Arbuzov's laboratory.

It seemed to me to be of interest to investigate the interaction of carbon tetrachloride and some alkyl esters of phosphorous acid. For that purpose, experiments were conducted which are described in short in the experimental part.

The experiments cited showed that carbon tetrachloride, when heated, reacts in an equimoler ratio with alkyl esters of pyrophosphorous acid under breaking of the bond at the oxygen bridge between the phosphorus atoms and formation of corresponding esters of trichloromethylphosphoric acid and of dialkyl phosphorous acid chlorides, according to the scheme:

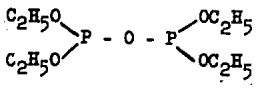


In addition to these two substances, the corresponding chlorides of dialkyl phosphoric acid were separated from the reaction mixture. The formation of the latter obviously did not take place as a consequence of oxidation, since the operation was carried out, from beginning to end, in an atmosphere of inert gas, but as the result of another course of the reaction:

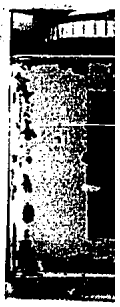


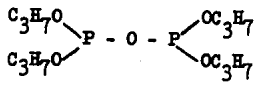
Experimental Part

The starting substances -- alkyl esters of pyrophosphorous acid -- were obtained by the method worked out by A. Ye. Arbuzov and his students (3) and had the following properties:

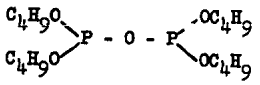


	Boiling point	n_D^{20}
	106 - 107°C at 11 mm	1.4338





147 - 148°C at 7 mm 1.4395



183 - 185°C at 11 mm 1.4448

The Action of Carbon Tetrachloride on Ethyl Ester of Phosphorous Acid

Fifty-three grams of ethyl ester of phosphorous acid and 31.6 grams of carbon tetrachloride were placed in a round-bottomed flask with reflux cooling. During heating of the contents of the flask on the water bath, a reaction, accompanied by the evolution of heat, set in, and the heating, therefore, had to be interrupted temporarily. At the end, the mixture was heated in a stream of carbon dioxide on a water bath for 2 hr. The flask with its contents was weighed before and after heating. No reduction in weight was observed.

After driving off a small quantity of carbon tetrachloride under normal pressure, the liquid which remained in the flask was distilled under vacuum.

Under a pressure of 16 mm, the following fractions were obtained:

Fraction I: 50-75°C, 16.8 g

Fraction II: 83-98°C, 12.9 g

Fraction III: 100-135°C, 20.4 g

Residue in the flask: 11.7 g

In redistillation, a substance was obtained from the first fraction, which boiled at 49-51°C at 14 mm pressure. According to the findings of the analysis, which included phosphorus, molecular refraction, and specific gravity determinations, the substance turned out to be diethyl phosphorous acid chloride.

After repeated distillation from an Arbuzov flask with a three-bulb fractionating column, a fraction was collected from the second fraction, which had a boiling point within the one-degree temperature range of 88-89°C at 15 mm pressure.

0.1057 g of substance; 33.1 ml of NaOH

0.1064 g of substance; 33.4 ml of NaOH

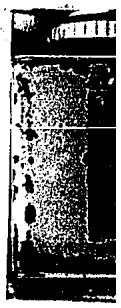
1 ml NaOH = 0.5686 g of P

Percentage of P found: 17.81; 17.85

Calculated percentage of P in $C_4H_{10}ClO_3P$: 17.98

Thus, according to the result of the analysis, the substance obtained is diethyl phosphorous acid chloride.

In redistillation of the third fraction, 7.9 g of substance were obtained, which boiled at 122-123.5°C at 12 mm pressure.



0.1056 g of substance; 22.8 ml NaOH

0.1086 g of substance; 23.5 ml NaOH

Percentage of P found: 12.27; 12.30

Calculated percentage of P in $C_5H_{10}Cl_3O_3P$: 12.15

$d_0^0 = 1.3851$, $d_0^{20} = 1.3616$, $n_D^{20} = 1.4589$

According to the findings of the investigation, the substance is identical with that obtained earlier (1), i.e., ethyl ester of trichloromethylphosphonic acid.

The Action of Carbon Tetrachloride on n-propyl Ester of Pyrophosphorous Acid

A mixture of 31 g of n-propyl ester of pyrophosphorous acid and 18 g of carbon tetrachloride were heated for 3 hr in a round-bottomed flask with reflux cooling in a stream of carbon dioxide. After removal of a small quantity of carbon tetrachloride, the remaining liquid was subjected to fractional distillation under vacuum:

Fraction I: 67-75°C, at 13-14 mm pressure, 8.2 g

Fraction II: 75-130°C, at 12 mm pressure, 6.3 g

Fraction III: 130-145°C, at 12 mm pressure, 10.1 g

In redistillation of the first fraction, pure pyrophosphorous acid chloride with a boiling point of 68-70°C at 12 mm pressure and n_D^{20} of 1.4409 was separated.

The analysis of the product separated after redistillation of the second fraction, which had a 106-107°C bp at 12 mm pressure, gave the following result:

0.1169 g of substance; 32.9 ml of NaOH

0.1085 g of substance; 30.4 ml of NaOH

1 ml NaOH = 0.5453 mg P

Percentage of P found: 15.34; 15.28

Calculated percentage of P in $C_6H_{14}ClO_3P$: 15.47

The data of the analysis for phosphorus shows that the substance separated is dipropyl phosphoric acid chloride.

In fractional distillation, a substance with a 144-145°C bp was separated from the third fraction:

0.1186 g of substance: 24.1 ml of NaOH

0.1001 g of substance; 20.2 ml of NaOH

Percentage of P found: 11.08; 11.01

Calculated percentage of P in $C_7H_{14}Cl_3O_3P$: 10.95

The substance obtained turned out to be n-propyl ester of Trichloromethylphosphonic acid.

$$d_0^0 = 1.2625, \quad d_0^{20} = 1.2454, \quad n_D^{20} = 1.4591$$

The Action of Carbon Tetrachloride on n-butyl Ester of Pyrophosphorous Acid

A mixture of 30 g n-butyl ester of pyrophosphorous acid and 25 g of carbon tetrachloride was heated for 4 hr in a flask with reflux cooling on a water bath.

After distilling off 6.1 g of carbon tetrachloride, the remaining liquid was distilled in a vacuum. The following three fractions were obtained:

Fraction I: 85-140°, at 15 mm pressure

Fraction II: 110-150°, at 15 mm pressure

Fraction III: 150-161°, at 15 mm pressure

By its physical and chemical properties, the first fraction suggested dibutyl phosphorous acid chloride.

On redistillation, a substance was separated from the third fraction with a 151-152°C bp at 10 mm pressure and n_D^{20} of 1.4523.

0.1047 g of substance, 18.85 g of NaOH

1 ml NaOH = 0.5642 mg P

Percentage of P found: 10.16

Calculated percentage of P in $C_9H_{18}Cl_3O_3P$: 9.96

According to the data of the analysis, the analyzed substance is entirely identical with that which we described earlier, i.e., n-butyl ester of trichloromethylphosphonic acid.

I wish to express my appreciation to O. N. Belorossova for her help in carrying out the experimental part of this work.

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